

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-185862  
(43)Date of publication of application : 02.07.2004

(51)Int.Cl.

H01M 10/36  
H01M 4/02  
H01M 4/04  
H01M 10/40

(21)Application number : 2002-348532

(71)Applicant : OHARA INC

(22)Date of filing : 29.11.2002

(72)Inventor : INDA YASUSHI

## (54) LITHIUM ION SECONDARY BATTERY AND ITS MANUFACTURING METHOD

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a safe lithium ion secondary battery having high capacity, high output, a long service life, and an excellent charge-discharge cycle life.

SOLUTION: This lithium ion secondary battery is provided with a positive electrode, a negative electrode, and a thin film-like solid electrolyte containing a lithium ion-conducting inorganic substance. The thin film-like solid electrolyte has a thickness below 20  $\mu\text{m}$ , is formed directly on an electrode material of the positive electrode and/or the negative electrode, has a lithium ion conductivity above 10 $^{-5}$  Scm $^{-1}$ , and contains 40 wt.% or more of lithium ion-conducting inorganic substance powder in a polymer medium. The average particle diameter of the inorganic substance powder is below 0.5  $\mu\text{m}$ . In this manufacturing method, the thin film-like solid electrolyte is formed by directly coating the electrode material of the positive electrode and/or the negative electrode with the lithium ion-conducting inorganic substance.



## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.

---

## CLAIMS

---

[Claim(s)]

[Claim 1]

A rechargeable lithium-ion battery which are an anode, a negative electrode, and a rechargeable lithium-ion battery provided with a solid electrolyte, and consists of a filmy solid electrolyte in which this solid electrolyte contains lithium ion conductivity mineral matter.

[Claim 2]

The rechargeable lithium-ion battery according to claim 1 in which this filmy solid electrolyte is 20 micrometers or less in thickness.

[Claim 3]

The rechargeable lithium-ion battery according to claim 1 or 2 with which this filmy solid electrolyte is directly formed on an electrode material of an anode and/or a negative electrode.

[Claim 4]

Lithium ion conductivity of this filmy solid electrolyte is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-3 which are more than  $10^{-5} \text{ Scm}^{-1}$ .

[Claim 5]

This filmy solid electrolyte is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-4 which contain mineral matter 40% of the weight or more.

[Claim 6]

This mineral matter is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-5 which consist of a lithium ion conductivity crystal.

[Claim 7]

This mineral matter is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-5 which consist of lithium ion conductivity glass.

[Claim 8]

This mineral matter is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-5 which consist of lithium-ion-conductivity crystallized glass.

[Claim 9]

This mineral matter is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-8 which consist of a mineral matter granular material.

[Claim 10]

The rechargeable lithium-ion battery according to claim 9 which is a granular material in which this mineral matter granular material consists of lithium-ion-conductivity crystallized glass.

[Claim 11]

The rechargeable lithium-ion battery according to claim 9 or 10 whose mean particle diameter of this mineral matter granular material is 1.0 micrometer or less.

[Claim 12]

This filmy solid electrolyte is a rechargeable lithium-ion battery given in any 1 paragraph among claims 9-11 which contain a lithium ion conductivity mineral matter granular material in a polymer medium.

[Claim 13]

This filmy solid electrolyte is a rechargeable lithium-ion battery given in any 1 paragraph among claims 9-12 which contain lithium mineral salt and a lithium conductivity crystallized glass granular material in a polymer medium.

## [Claim 14]

This **filmy solid electrolyte** is a rechargeable lithium-ion battery given in any 1 paragraph among claims 3-13 directly formed by coating on an electrode material of an anode and/or a negative electrode.

## [Claim 15]

This **filmy solid electrolyte** is a rechargeable lithium-ion battery given in any 1 paragraph among claims 3-14 which consist of lithium-ion-conductivity crystallized glass obtained by crystallizing an amorphous layer directly formed by coating on an electrode material of an anode and/or a negative electrode.

## [Claim 16]

It is a rechargeable lithium-ion battery given in any 1 paragraph among claims 1-15 which are an anode, a negative electrode, and the rechargeable lithium-ion battery provided with a solid electrolyte, and contain a lithium ion conductivity mineral matter granular material in this anode and/or this negative electrode.

## [Claim 17]

The rechargeable lithium-ion battery according to claim 16 whose mean particle diameter of this mineral matter granular material contained in this anode and/or this negative electrode is 3 micrometers or less.

## [Claim 18]

It is a manufacturing method of a rechargeable lithium-ion battery provided with a **filmy solid electrolyte** containing lithium ion conductivity mineral matter. A manufacturing method of a rechargeable lithium-ion battery forming a **filmy solid electrolyte** by coating lithium ion conductivity mineral matter directly on an electrode material of an anode and/or a negative electrode.

## [Claim 19]

A manufacturing method of the rechargeable lithium-ion battery according to claim 18 which prepares a slurry containing lithium ion conductivity mineral matter, and is characterized by forming a **filmy solid electrolyte** by coating this slurry directly on an electrode material of an anode and/or a negative electrode.

## [Claim 20]

A manufacturing method of the rechargeable lithium-ion battery according to claim 18 which coats lithium ion conductivity mineral matter directly, forms an amorphous layer on an electrode material of an anode and/or a negative electrode, and is characterized by considering it as a **filmy solid electrolyte** by crystallizing this amorphous layer.

---

[Translation done.]

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

#### [0001]

#### [Field of the Invention]

This invention relates to a rechargeable lithium-ion battery which used the filmy solid electrolyte, and a manufacturing method for the same.

#### [0002]

#### [Description of the Prior Art]

[Patent documents 1] JP,2000-067917,A

[Patent documents 2] JP,2001-015164,A

[Patent documents 3] JP,07-326372,A

Although the electrolysis solution of the non-drainage system was generally used as an electrolysis solution in a rechargeable lithium-ion battery from the former, a fluid replaces a central electrolysis solution in this way in recent years, and the rechargeable lithium-ion battery using the polymer electrolyte which comprised polymers came to attract attention.

[Patent documents 1] .Namely, in the rechargeable lithium-ion battery using the polymer electrolyte in this way, Since the electrolysis solution of a fluid was held in a polymer electrolyte, it was hard to carry out a liquid spill, there was also little corrosiveness, the short circuit of the electrode by generating of a lithium deposit (dendrite) was prevented, and the structure of the cell was easy and there was an advantage, like the assembly also becomes easy.

#### [0003]

Here, since such a polymer electrolyte has the low conductivity of a lithium ion only compared with an electrolysis solution, making thickness of this polymer electrolyte thin came to be performed. However, when a polymer electrolyte was made thin in this way, the mechanical strength became low, it was torn at the time of production of a cell, or the hole opened, the polymer electrolyte was destroyed, and there was a problem of being easy to short-circuit an anode and a negative electrode. As thickness of a gel polymer electrolyte layer, it is introduced with about 30-80 micrometers.

#### [0004]

It is the purpose of improving a mechanical strength and is a lithium ion conductivity crystallized glass granular material.

The compound electrolyte to contain is also proposed.

[Patent documents 2] .However, 20 micrometers or less-thick thin film-ization was not realized.

#### [0005]

Many solid electrolyte cells which do not use an electrolysis solution at all are also proposed. In the rechargeable lithium-ion battery using a solid electrolyte, since organic electrolysis liquid does not need to be impregnated like the conventional cell, there is no danger of causing liquid leakage, ignition, etc., and a cell with high safety may be able to provide.

[Patent documents 3] .In the cell using conventional organic electrolysis liquid, since the anode and the negative electrode touched with organic electrolysis liquid via a solid electrolyte, the ion migration resistance by an interface did not become a problem so much. However, when all of the anode, negative electrode, and electrolyte which are constituted are solids, as compared with the cell using an electrolysis solution, the interface of an anode-electrolyte and the interface of a negative-electrode-electrolyte become contact of solids, and a partial target with contact at a point, and big interfacial resistance arises. Therefore, the impedance in the interface was

large, it becomes easy to cause polarization, and lithium ion movement of the interface was restricted, it was hard to realize and the cell of high capacity and high power was cut.

[0006]

[Problem(s) to be Solved by the Invention]

Also in the case where make for this invention to solve the above problems in a rechargeable lithium-ion battery into a technical problem, and a solid electrolyte is used, Since [ that an electrolyte is thin ] resistance is small, a charge-discharge cycle characteristic also makes it a technical problem to provide the good rechargeable lithium-ion battery which can use being stabilized in the long run with high power and high capacity.

[0007]

[Means for Solving the Problem]

As a result of this invention persons' experimenting in detail about various materials as a rechargeable lithium-ion battery use, mineral matter which has a certain crystal has high lithium ion conductivity, and the lithium ion transference number is 1, When this material was made filmy and used as a solid electrolyte of a rechargeable lithium-ion battery, it found out that a highly efficient cell could be provided.

[0008]

A rechargeable lithium-ion battery of this invention is provided with an anode, a negative electrode, and a solid electrolyte, and a solid electrolyte consists of a filmy solid electrolyte containing lithium ion conductivity mineral matter. As for a filmy solid electrolyte, it is preferred that containing lithium ion conductivity high mineral matter contains lithium ion conductivity desirable still more desirable crystal, glass, or crystallized glass. Since a high-output cell is obtained since the thinner one of migration length of a lithium ion is short, and an electrode area per unit volume can secure widely a filmy solid electrolyte used for a rechargeable lithium-ion battery of this invention, a cell of high capacity is obtained. Then, in a rechargeable lithium-ion battery of this invention, as for thickness of a filmy solid electrolyte, 20 micrometers or less are preferred, its 10 micrometers or less are more preferred, and especially its 5 micrometers or less are preferred.

[0009]

It depends for the mobility of a lithium ion at the time of charge and discharge of a rechargeable lithium-ion battery of this invention on lithium ion conductivity and the lithium ion transference number of a solid electrolyte. Therefore, as for ionic conductivity of a filmy solid electrolyte, in a rechargeable lithium-ion battery of this invention, it is preferred that it is more than  $1 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ .

[0010]

As for this filmy solid electrolyte, in a rechargeable lithium-ion battery of this invention, it is preferred to contain mineral matter 40% of the weight or more. As for this mineral matter, it is preferred to consist of lithium ion conductivity crystal, glass, or crystallized glass. As for this mineral matter, consisting of a mineral matter granular material is preferred. As for mean particle diameter of this mineral matter granular material contained in this filmy solid electrolyte, it is preferred that it is 1.0 micrometer or less, its 0.5 micrometer or less is more preferred, and especially its 0.3 micrometer or less is preferred.

[0011]

In a rechargeable lithium-ion battery of this invention, this filmy solid electrolyte can contain a lithium ion conductivity mineral matter granular material in a polymer medium. As for this filmy solid electrolyte, it is preferred to contain lithium mineral salt and a lithium conductivity crystallized glass granular material in a polymer medium.

[0012]

In a rechargeable lithium-ion battery of this invention, this filmy solid electrolyte can be directly formed by coating on an electrode material of an anode and/or a negative electrode.

[0013]

A manufacturing method of a rechargeable lithium-ion battery of this invention, A filmy solid electrolyte is formed by being a manufacturing method of a rechargeable lithium-ion battery provided with a filmy solid electrolyte containing lithium ion conductivity mineral matter, and coating lithium ion conductivity mineral matter directly on an electrode material of an anode and/or a negative electrode.

[0014]

Since the thinner one of resistance is low and migration length of a solid electrolyte of ion is short, a high power cell is obtained, but when manufacturing these independently, there is a limit in making it thin from a problem of intensity and handling, and a manufacturing process. On the other hand, in a manufacturing method of a

rechargeable lithium-ion battery of this invention, since a solid electrolyte is directly formed on an electrode material of an anode and/or a negative electrode, since it is not generated, problems, such as handling independently, can be made still thinner.

[0015]

In a rechargeable lithium-ion battery of this invention, a filmy solid electrolyte prepares a slurry which contains lithium ion conductivity crystal, glass, or crystallized glass as mineral matter, and can produce it by coating this slurry directly on an electrode material of an anode and/or a negative electrode.

[0016]

As a method of coating a slurry directly on an electrode material of an anode and/or a negative electrode, Printing technique, such as methods, such as dip, spin coating, and tape casting, an ink jet, and screen-stencil, can be used, and what distributed with a binder powder which has lithium ion conductivity in a solvent can be used for a slurry as mineral matter. As for mineral matter, it is preferred to consist of a crystal, glass, or crystallized glass. As for this filmy solid electrolyte, it is preferred to contain mineral matter 40% of the weight or more.

[0017]

Here, as for lithium ion conductivity powder to be used, it is preferred to have high lithium ion conductivity. It is stable crystallized glass chemically still more preferably, and mother glass is specifically the presentation of a  $\text{Li}_2\text{O}$ -aluminum<sub>2</sub> $\text{O}_3$ - $\text{TiO}_2$ - $\text{SiO}_2$ - $\text{P}_2\text{O}_5$  system, Heat-treat this glass, it is made to crystallize, and a main crystal phase in that case is the powder which is  $\text{Li}_{1-x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$  ( $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ).

[0018]

Since a binder to be used makes an electrode which are a crystal, glass or crystallized glass powder, and a substrate bind, it is preferred to use a charge of an organic high polymer material. As a concrete material, polyethylene oxide, polyethylene, polypropylene, Polymer materials, such as fluoro-resins, such as polyolefine, polytetrafluoroethylene, polychlorotrifluoroethylene resin, and polyvinylidene fluoride, polyamide, and polyester polyacrylate, and a polymer material which has these as a structural unit can be used. Since the ion conductivity of a compound electrolyte will also become high if a polymer material which added lithium salt etc. and to which lithium ion conductivity was made to add is used or it uses a binder which has lithium ion conductivity, it is more desirable. As a solvent, an organic solvent which the above-mentioned polymer material dissolves or distributes can be used.

[0019]

In a rechargeable lithium-ion battery of this invention, a filmy solid electrolyte is also producible by coating lithium ion conductivity mineral matter directly on an electrode material. As a method of coating mineral matter directly on an electrode material, known thin film manufacturing devices, such as sputtering process, a laser ablation method, and a plasma metal spray, can also be used. Under the present circumstances, a thin film can be directly formed on an electrode material using a composite material which contained a lithium ion conductivity crystal, glass, or a crystal and glass of these lithium ion conductivity at a target.

[0020]

Here, it is preferred to use lithium ion conductivity stable and high crystallized glass for a target material chemically [ the above ]. When it thin-film-izes, it may become amorphous, but by heat-treating in this case and crystallizing, if the above-mentioned main crystal phase is deposited, it will be satisfactory. Mother glass before crystallization of this crystallized glass can be similarly used as a target. The above-mentioned main crystal phase is obtained by performing crystallization treatment, after forming membranes also in this case. A target of a composite material adds an inorganic binder to a lithium ion conductivity crystal, glass, and crystallized glass powder, calcinates it, and is obtained. As a crystallized glass granular material, it is preferred here to have lithium ion conductivity, and it is more preferred that a main crystal phase is  $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ . As mean particle diameter of this crystallized glass granular material, 5 micrometers or less are preferred, and 3 micrometers or less are more preferred. As for an inorganic binder to be used, it is preferred that it is a crystal and glass which are the inorganic oxides of a low melting point, and less than 20wt% of quantity is preferred.

[0021]

In a rechargeable lithium-ion battery using a thin film solid electrolyte of this invention, a thing in which material which contains a transition metal oxide as positive active material in aluminium foil as a positive pole collector, etc. was formed can be used as an anode. As a positive-active-material material used for an anode of a rechargeable lithium-ion battery of this invention, An oxide which can use occlusion of lithium and a transition

metal compound which can be emitted, for example, is chosen from transition metals, such as manganese, cobalt, iron, nickel, vanadium, niobium, molybdenum, and titanium, and which contains a kind at least can be used. When using for negative electrode active material material which does not contain lithium, it is preferred to use a lithium containing transition metal oxide.

[0022]

In a rechargeable lithium-ion battery using a thin film solid electrolyte of this invention, lithium ion conductivity mineral matter is contained in this filmy solid electrolyte, and it is preferred to contain lithium ion conductivity mineral matter as an ion conduction auxiliary agent also in an anode. It is preferred that a main crystal phase uses crystallized glass powder which is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$  as lithium ion conductivity mineral matter used here like mineral matter contained in this filmy solid electrolyte. As mean particle diameter of a crystallized glass granular material used here, 5 micrometers or less are preferred and 3 micrometers or less are more preferred.

[0023]

In a rechargeable lithium-ion battery using a thin film solid electrolyte of this invention, it is preferred to an anode to contain an electric conduction auxiliary agent and/or a binder. As an electric conduction auxiliary agent, acetylene black is preferred, and the polyvinylidene fluoride PVdF is preferred as a binder.

[0024]

In a rechargeable lithium-ion battery of this invention, a thing in which material which contains negative electrode active material in copper foil as a negative pole collector, etc. was formed can be used as a negative electrode. As a negative-electrode-active-material material used for a negative electrode of a rechargeable lithium-ion battery of this invention, Material of carbon systems, such as transition metal oxides, such as occlusion of lithium, such as metal lithium, a lithium aluminum alloy, a lithium indium alloy, metal and an alloy which can be emitted, titanium, and vanadium, black lead, activated carbon, mesophase pitch carbon fiber, can be used.

[0025]

In a rechargeable lithium-ion battery of this invention, lithium ion conductivity mineral matter is contained in this filmy solid electrolyte, and it is preferred to contain lithium ion conductivity mineral matter as an ion conduction auxiliary agent also in a negative electrode. As lithium ion conductivity mineral matter used here, It is preferred that a main crystal phase uses crystallized glass powder which is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$  like mineral matter contained in this filmy solid electrolyte. This negative electrode can be prepared by mixing negative-electrode-active-material material, an ion conduction auxiliary agent, and a binder using an acetone solvent, and applying this mixture on a negative pole collector. Commercial graphite powder can be used for negative electrode active material.

[0026]

A concrete example is hereafter given and described about a lithium ion battery using a thin film solid electrolyte and this concerning this invention, and a comparative example is given and a point that a rechargeable lithium-ion battery provided with a thin film solid electrolyte concerning this invention is excellent is clarified. A rechargeable lithium-ion battery of this invention is not limited to what was shown in the following example, in a range which does not change the gist, is changed suitably and can be carried out.

[0027]

[Embodiment of the Invention]

(Example 1)

(Production of an anode)

To positive active material, using commercial cobalt-acid-lithium  $LiCoO_2$ , this positive-active-material material, Acetylene black which is an electric conduction auxiliary agent, and the crystallized glass powder whose main crystal phase it is an ion conduction auxiliary agent and is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$ , The polyvinylidene fluoride PVdF which is a binder is mixed using an acetone solvent, After applying this mixture so that thickness may be set to about 50 micrometers on the 10-micrometer-thick positive pole collector which is an aluminium sheet, the positive electrode sheet which dried this at the temperature of 100 \*\* and became a sheet shaped was produced. Here, as crystallized glass powder, mean particle diameter used a 1.0 micrometer (volume average) thing, and the maximum droplet size used an 8-micrometer thing. Particle diameter was measured with laser diffraction / scatter type particle size distribution measuring device.

[0028]

## (Production of a negative electrode)

Crystallized glass powder which is this negative-electrode-active-material material and an ion conduction auxiliary agent using the graphite powder of marketing to negative electrode active material (as well as what was used for production of an anode) A main crystal phase is  $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , and 1.0 micrometer and a maximum droplet size mean particle diameter 8 micrometers, The polyvinylidene fluoride PVdF which is a binder was mixed using the acetone solvent, and after applying this mixture so that thickness may be set to about 50 micrometers on the 10-micrometer-thick negative pole collector which is a copper sheet, the negative electrode sheet which dried this at the temperature of 100 \*\* and became a sheet shaped was produced.

[0029]

## (Production of a filmy solid electrolyte, and assembly of a cell)

A main crystal phase is  $\text{Li}_{1+x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ , and 0.15 micrometer and a maximum droplet size mean particle diameter 0.3-micrometer crystallized glass powder, Acetone was uniformly mixed for the polyethylene oxide which added  $\text{LiBF}_4$  as lithium salt as a solvent. The active material [ of the positive electrode sheet which produced this mixture above ], and active material side of a negative electrode sheet applied to each, and also acetone which is a solvent was dried and removed, and the filmy solid electrolyte layer was directly formed on the electrode material of an anode and a negative electrode. Where the spreading side of an anode and a negative electrode sheet is pasted together, it started in through and size of 40x50 mm at the roll press, and the rechargeable lithium-ion battery shown in drawing 1 in which the filmy solid electrolyte was formed between the anode and the negative electrode was assembled. The whole thickness of this cell was 110 micrometers, and the thickness of the filmy solid electrolyte layer was 3 micrometers in it.

The lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test of 25 \*\* and 4.2V-3.5V was done. The cycle characteristic of the service capacity to 20 cycles was shown in drawing 2. The initial service capacity of Example 1 is 36.2mAh, and after 20 cycles was maintaining 34.1mAh and not less than 96% of initial capacity.

[0030]

## (Comparative example 1)

Except not using crystallized glass powder for a filmy solid electrolyte, the same cell as Example 1 was constructed, and the charge-and-discharge cycle test was done on the same conditions. The cycle characteristic of the service capacity to 20 cycles was shown in drawing 2.

[0031]

## (Example 2)

Commercial cobalt-acid-lithium  $\text{LiCoO}_2$  is used for positive active material, The same positive-active-material material as Example 1, the electric conduction auxiliary agent, the ion conduction auxiliary agent, and the binder were mixed using the acetone solvent, this mixture was applied so that thickness might be set to about 50 micrometers on the 10-micrometer-thick positive pole collector which is an aluminium sheet, and it was considered as the positive electrode layer. after that -- immediately -- production of the filmy solid electrolyte of Example 1 -- the same -- the mixture of the polyethylene oxide which added crystallized glass powder and lithium salt was thinly applied on this positive electrode layer, and was made into the electrolyte layer.

Continuously, the same mixture as production of the negative electrode of Example 1 was applied so that thickness might be set to about 50 micrometers on an electrolyte layer. After pasting together to the negative-electrode spreading side the copper sheet which is a negative pole collector and making it dry at 100 \*\*, it started in through and size of 40x50 mm at the roll press, and the rechargeable lithium-ion battery shown in drawing 1 in which the filmy solid electrolyte was formed between the anode and the negative electrode was assembled. The thickness of this whole cell was 100 micrometers, and the thickness of the filmy solid electrolyte layer was about 2 micrometers in it. Since the spreading of an anode-electrolyte-negative electrode cannot enter a drying process on the way, in each interface, the anode, the solid electrolyte layer, and a solid electrolyte and a negative electrode layer have been mixed by it.

[0032]

The lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test of 4.2V-3.5V was done in the constant current of 25 \*\* and  $0.1 \text{ mA/cm}^2$ . The rapid charge-and-discharge cycle test was also done in the constant current of  $1 \text{ mA/cm}^2$ .

[0033]

## (Comparative example 2)

Except not using crystallized glass powder for a filmy solid electrolyte, the same cell as Example 2 was constructed, and the charge-and-discharge cycle test was done on the same conditions. Comparison of 0.1 and the initial service capacity in the charge-and-discharge density of 1 mA/cm<sup>2</sup>, and the service capacity after 20 cycles was shown in Table 1.

[0034]

[Table 1]

	実施例2		比較例2	
	0.1mA/cm <sup>2</sup>	1mA/cm <sup>2</sup>	0.1mA/cm <sup>2</sup>	1mA/cm <sup>2</sup>
初期放電容量(mAh)	39.2	38.8	35.0	32.2
20サイクル後の放電容量(mAh)	36.3	35.1	31.2	26.5

[0035]

As shown in Table 1, the fall of the service capacity by degradation according [ the cell of Example 2 ] to a cycle and rapid charge and discharge was suppressed small.

[0036]

(Example 3)

The same crystallized glass powder as what was used for production of the anode of Example 1 (a main crystal phase is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$ , and) After mean particle diameter carried out pressing of the 1.0 micrometer to the shape of a disk by using lithium phosphate  $Li_3PO_4$  as an inorganic binder, it was calcinated and obtained the target material. The periphery and both sides of the target material which were acquired were ground and ground, and the sputtering target (100 mm in diameter and 1 mm in thickness) was obtained.

[0037]

With RF magnetron sputtering equipment, the thin film was formed on phi20mm and the 20-micrometer-thick lithium aluminum alloy foil of a negative electrode. The solid electrolyte layer obtained at this time was 0.1 micrometer in thickness. Next, on this filmy solid electrolyte,  $LiCoO_2$  which is a positive electrode material was formed with the sputter device. The positive electrode film obtained at this time was 2 micrometers in thickness. Aluminum which is a positive pole collector on it was formed in thickness of 0.1 micrometer. Since the solid electrolyte and the positive electrode film were made amorphous, they heat-treated at 550 \*\* and were used as the thin film cell about 22 micrometers thick. This cell was pierced to phi18mm, and it put into the phi20mm coin cell, and finished setting up a coin type cell.

[0038]

-The charge-and-discharge cycle test of 3.5V-2.5V was done according to the constant current of 1 mA/cm<sup>2</sup> at each temperature of 20 \*\*, 25 \*\*, and 80 \*\*. The coin type cell which it finished setting up was mounted in the circuit board by a 250 \*\* solder reflow, and the same cycle test was done at 25 \*\*.

[0039]

(Comparative example 3)

The cell as for which the electrolyte impregnated the nonwoven fabric with the electrolysis solution as usual was produced. The anode formed  $LiCoO_2$  with the sputter device like Example 1 on the 10-micrometer aluminium foil in thickness using the lithium aluminum alloy as Example 1 with same negative electrode. An anode and a negative electrode are pasted together via the separator of a 26-micrometer-thick nonwoven fabric. It impregnated there with the propylene carbonate which added  $LiN(C_2F_5SO_2)_2$  as a lithium supporting electrolyte, was considered as the filmy cell about 58 micrometers thick, and finished setting up a coin type cell like Example 3 except the above. The charge-and-discharge cycle test was done on the same conditions as Example 3.

Comparison of the service capacity after the first stage after the initial service capacity at each temperature, the

service capacity after 300 cycles, and a solder reflow and 300 cycles was shown in Table 2.

[0040]

[Table 2]

	実施例3		比較例3	
	初期容量 (mAh)	300Cycle 後 の容量 (mAh)	初期容量 (mAh)	300Cycle 後 の容量 (mAh)
-25°C	0.12	0.11	0.05	0.02
25°C	0.22	0.20	0.22	0.16
80°C	0.24	0.19	0.22	0.12
25°C (ハンダリフ ロー)	0.21	0.18	破裂	-

[0041]

From Table 2, the cell of Example 3 has a good cycle characteristic at each temperature, and was maintaining about 50% of capacity also in -25 \*\* as compared with room temperature use. Although the cell of the comparative example 3 exploded by a solder reflow, the cell of Example 3 hardly caused capacity deterioration.

[0042]

(Example 4)

(Production of an anode)

The positive electrode layer and the thin electrolyte layer were produced on aluminum of a positive pole collector like Example 2 except the point of having used  $\text{LiMn}_2\text{O}_4$  for positive active material.

[0043]

(Production of a negative electrode)

Use  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  for negative electrode active material, and This negative-electrode-active-material material, The polyvinylidene fluoride PVdF which is a binder is mixed with the crystallized glass powder which is an ion conduction auxiliary agent using an acetone solvent, This mixture was applied so that thickness might be set to about 50 micrometers on the 10-micrometer-thick negative pole collector which is a copper sheet, and the negative electrode layer was produced on copper of a negative pole collector. after that -- immediately -- production of the filmy solid electrolyte of Example 1 -- the same -- the mixture of the polyethylene oxide which added crystallized glass powder and lithium salt was thinly applied on this negative electrode layer, and the thin electrolyte layer was produced.

[0044]

(Assembly of a cell)

Both the electrolyte sides of an anode and a negative electrode are pasted together, at 100 \*\*, it let it pass to the roll press, and it was dried. The thickness of 60 micrometers and a filmy solid electrolyte layer of the thickness of the positive electrode layer was 100 micrometers in thickness of 3 micrometers and a negative electrode layer, and the whole thickness was about 180 micrometers. It started in size of 40x50 mm, the lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test of 3.0V-2.2V was done in the constant current of 25 \*\* and  $0.1 \text{ mA/cm}^2$ .

[0045]

(Comparative example 4)

Except not using crystallized glass powder for the electrolyte layer of an anode and a negative electrode, the same cell as Example 4 was constructed, and the charge-and-discharge cycle test was done on the same conditions. The cycle characteristic of the service capacity to 20 cycles was shown in drawing 3. Although the initial service capacity of Example 4 was a value somewhat lower than the comparative example 4, there was little degradation of a subsequent cycle characteristic and 20 cycles after was maintaining 98% of early capacity.

[0046]

(Example 5)

The same cell as Example 4 was produced and the charge-and-discharge cycle test of 3.0V-2.2V was done at 25 \*\* by the rapid charge and discharge of the constant current of  $0.1 \text{ mA/cm}^2$  and 1, and  $3 \text{ mA/cm}^2$ .

[0047]

(Comparative example 5)

Acetone is uniformly mixed for crystallized glass powder and the polyethylene oxide which added  $\text{LiBF}_4$  as lithium salt as a solvent, This mixture was applied to a thickness of 50 micrometers on the cast sheet, this was dried, it applied to the roll press, and the sheet shaped 30-micrometer-thick solid electrolyte was produced. The negative electrode layer was produced on the positive electrode layer and the negative pole collector of a copper sheet on aluminum of a positive pole collector like Example 4. And the positive electrode layer and the negative electrode layer were pasted together to both sides of a sheet-shaped solid electrolyte (separator), it applied to the roll press, and the sheet shaped 210-micrometer-thick cell was produced. It started in size of 40x50 mm, the lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test was done on the same conditions as Example 4. Initial service capacity and the service capacity after 20 cycles were shown in Table 3.

[0048]

[Table 3]

充放電密度	実施例5		比較例5	
	初期容量 (mAh)	20Cycle 後の容量 (mAh)	初期容量 (mAh)	20Cycle 後の容量 (mAh)
$0.1 \text{ mA/cm}^2$	32.0	31.3	30.8	29.0
$1 \text{ mA/cm}^2$	32.0	31.1	25.3	23.1
$3 \text{ mA/cm}^2$	31.5	30.3	20.4	16.5

[0049]

Although there was no difference at the charge-and-discharge speed about  $0.1 \text{ mA/cm}^2$  with a big cell of Example 5 and the comparative example 5, when charge-and-discharge density was raised and rapid charge and discharge were performed, reduction of capacity carried out clearly has been checked by the comparative example 5. This is the cause that resistance of the ion migration in the interface of the anode-solid electrolyte of a cell and a solid electrolyte-negative electrode is big. The solid electrolyte was directly formed in the electrode and the cell which is equal also to a big output was obtained in Example 5 which reduced interfacial resistance.

[0050]

[Effect of the Invention]

As mentioned already, the rechargeable lithium-ion battery provided with the filmy solid electrolyte of this invention was high power, and its charge-discharge cycle characteristic was also good. Since organic electrolysis liquid was not included as compared with the conventional rechargeable lithium-ion battery, the safe and long lasting cell was realized.

The rechargeable battery provided with the conventional solid electrolyte receives, although the electrochemical resistance by the interface of an anode-electrolyte or the interface of a negative-electrode-electrolyte is strong. By forming a solid electrolyte directly on an electrode, contact of the interface of an anode and a negative electrode, and a solid electrolyte becomes good, and the rechargeable battery of high capacity and high power of the rechargeable lithium-ion battery provided with the filmy solid electrolyte of this invention becomes possible.

[0051]

In the rechargeable lithium-ion battery, when an electrolyte is made extremely thin, and stress is added to a cell or it bends, the short circuit by an internal short circuit, etc. have been regarded as questionable, but. In the rechargeable lithium-ion battery provided with the filmy solid electrolyte of this invention, since a lot of mineral matter in a solid electrolyte, such as crystallized glass particles, exists, in order that an internal short circuit may

not break out by external force, it does not become a problem. When [ all ] a filmy solid electrolyte is formed by weld slag etc., it can be considered as crystallized glass and a possibility of connecting too hastily can be made for there to be nothing.

[Brief Description of the Drawings]

[Drawing 1]The section explanatory view showing the internal structure of the rechargeable lithium-ion battery of this invention.

[Drawing 2]Change of the service capacity accompanying the charging and discharging cycle of the rechargeable lithium-ion battery obtained by Example 1 and the comparative example 1.

[Drawing 3]Change of the service capacity accompanying the charging and discharging cycle of the rechargeable lithium-ion battery obtained by Example 4 and the comparative example 4.

[Description of Notations]

1. Positive pole collector
2. Anode
3. Filmy solid electrolyte
4. Negative electrode
5. Negative pole collector

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any  
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

**[Field of the Invention]**

This invention relates to a rechargeable lithium-ion battery which used the filmy solid electrolyte, and a manufacturing method for the same.

[0002]

---

[Translation done.]

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

PRIOR ART

## [Description of the Prior Art]

- [Patent documents 1] JP,2000-067917,A
- [Patent documents 2] JP,2001-015164,A
- [Patent documents 3] JP,07-326372,A

Although the electrolysis solution of the non-drainage system was generally used as an electrolysis solution in a rechargeable lithium-ion battery from the former, a fluid replaces a central electrolysis solution in this way in recent years, and the rechargeable lithium-ion battery using the polymer electrolyte which comprised polymers came to attract attention.

[Patent documents 1] .Namely, in the rechargeable lithium-ion battery using the polymer electrolyte in this way, Since the electrolysis solution of a fluid was held in a polymer electrolyte, it was hard to carry out a liquid spill, there was also little corrosiveness, the short circuit of the electrode by generating of a lithium deposit (dendrite) was prevented, and the structure of the cell was easy and there was an advantage, like the assembly also becomes easy.

## [0003]

Here, since such a polymer electrolyte has the low conductivity of a lithium ion only compared with an electrolysis solution, making thickness of this polymer electrolyte thin came to be performed. However, when a polymer electrolyte was made thin in this way, the mechanical strength became low, it was torn at the time of production of a cell, or the hole opened, the polymer electrolyte was destroyed, and there was a problem of being easy to short-circuit an anode and a negative electrode. As thickness of a gel polymer electrolyte layer, it is introduced with about 30-80 micrometers.

## [0004]

It is the purpose of improving a mechanical strength and is a lithium ion conductivity crystallized glass granular material.

The compound electrolyte to contain is also proposed.

[Patent documents 2] .However, 20 micrometers or less-thick thin film-ization was not realized.

## [0005]

Many solid electrolyte cells which do not use an electrolysis solution at all are also proposed. In the rechargeable lithium-ion battery using a solid electrolyte, since organic electrolysis liquid does not need to be impregnated like the conventional cell, there is no danger of causing liquid leakage, ignition, etc., and a cell with high safety may be able to provide.

[Patent documents 3] .In the cell using conventional organic electrolysis liquid, since the anode and the negative electrode touched with organic electrolysis liquid via a solid electrolyte, the ion migration resistance by an interface did not become a problem so much. However, when all of the anode, negative electrode, and electrolyte which are constituted are solids, as compared with the cell using an electrolysis solution, the interface of an anode-electrolyte and the interface of a negative-electrode-electrolyte become contact of solids, and a partial target with contact at a point, and big interfacial resistance arises. Therefore, the impedance in the interface was large, it becomes easy to cause polarization, and lithium ion movement of the interface was restricted, it was hard to realize and the cell of high capacity and high power was cut.

## [0006]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

**[Effect of the Invention]**

As mentioned already, the rechargeable lithium-ion battery provided with the filmy solid electrolyte of this invention was high power, and its charge-discharge cycle characteristic was also good. Since organic electrolysis liquid was not included as compared with the conventional rechargeable lithium-ion battery, the safe and long lasting cell was realized.

The rechargeable battery provided with the conventional solid electrolyte receives, although the electrochemical resistance by the interface of an anode-electrolyte or the interface of a negative-electrode-electrolyte is strong. By forming a solid electrolyte directly on an electrode, contact of the interface of an anode and a negative electrode, and a solid electrolyte becomes good, and the rechargeable battery of high capacity and high power of the rechargeable lithium-ion battery provided with the filmy solid electrolyte of this invention becomes possible.

[0051]

In the rechargeable lithium-ion battery, when an electrolyte is made extremely thin, and stress is added to a cell or it bends, the short circuit by an internal short circuit, etc. have been regarded as questionable, but. In the rechargeable lithium-ion battery provided with the filmy solid electrolyte of this invention, since a lot of mineral matter in a solid electrolyte, such as crystallized glass particles, exists, in order that an internal short circuit may not break out by external force, it does not become a problem. When [ all ] a filmy solid electrolyte is formed by weld slag etc., it can be considered as crystallized glass and a possibility of connecting too hastily can be made for there to be nothing.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

**[Problem(s) to be Solved by the Invention]**

Also in the case where make for this invention to solve the above problems in a rechargeable lithium-ion battery into a technical problem, and a solid electrolyte is used, Since [ that an electrolyte is thin ] resistance is small, a charge-discharge cycle characteristic also makes it a technical problem to provide the good rechargeable lithium-ion battery which can use being stabilized in the long run with high power and high capacity.

[0007]

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**MEANS**

---

**[Means for Solving the Problem]**

As a result of this invention persons' experimenting in detail about various materials as a rechargeable lithium-ion battery use, mineral matter which has a certain crystal has high lithium ion conductivity, and the lithium ion transference number is 1, When this material was made filmy and used as a solid electrolyte of a rechargeable lithium-ion battery, it found out that a highly efficient cell could be provided.

**[0008]**

A rechargeable lithium-ion battery of this invention is provided with an anode, a negative electrode, and a solid electrolyte, and a solid electrolyte consists of a filmy solid electrolyte containing lithium ion conductivity mineral matter. As for a filmy solid electrolyte, it is preferred that containing lithium ion conductivity high mineral matter contains lithium ion conductivity desirable still more desirable crystal, glass, or crystallized glass. Since a high-output cell is obtained since the thinner one of migration length of a lithium ion is short, and an electrode area per unit volume can secure widely a filmy solid electrolyte used for a rechargeable lithium-ion battery of this invention, a cell of high capacity is obtained. Then, in a rechargeable lithium-ion battery of this invention, as for thickness of a filmy solid electrolyte, 20 micrometers or less are preferred, its 10 micrometers or less are more preferred, and especially its 5 micrometers or less are preferred.

**[0009]**

It depends for the mobility of a lithium ion at the time of charge and discharge of a rechargeable lithium-ion battery of this invention on lithium ion conductivity and the lithium ion transference number of a solid electrolyte. Therefore, as for ionic conductivity of a filmy solid electrolyte, in a rechargeable lithium-ion battery of this invention, it is preferred that it is more than  $1 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ .

**[0010]**

As for this filmy solid electrolyte, in a rechargeable lithium-ion battery of this invention, it is preferred to contain mineral matter 40% of the weight or more. As for this mineral matter, it is preferred to consist of lithium ion conductivity crystal, glass, or crystallized glass. As for this mineral matter, consisting of a mineral matter granular material is preferred. As for mean particle diameter of this mineral matter granular material contained in this filmy solid electrolyte, it is preferred that it is 1.0 micrometer or less, its 0.5 micrometer or less is more preferred, and especially its 0.3 micrometer or less is preferred.

**[0011]**

In a rechargeable lithium-ion battery of this invention, this filmy solid electrolyte can contain a lithium ion conductivity mineral matter granular material in a polymer medium. As for this filmy solid electrolyte, it is preferred to contain lithium mineral salt and a lithium conductivity crystallized glass granular material in a polymer medium.

**[0012]**

In a rechargeable lithium-ion battery of this invention, this filmy solid electrolyte can be directly formed by coating on an electrode material of an anode and/or a negative electrode.

**[0013]**

A manufacturing method of a rechargeable lithium-ion battery of this invention, A filmy solid electrolyte is formed by being a manufacturing method of a rechargeable lithium-ion battery provided with a filmy solid electrolyte containing lithium ion conductivity mineral matter, and coating lithium ion conductivity mineral matter directly on an electrode material of an anode and/or a negative electrode.

**[0014]**

Since the thinner one of resistance is low and migration length of a solid electrolyte of ion is short, a high power

cell is obtained, but when manufacturing these independently, there is a limit in making it thin from a problem of intensity and handling, and a manufacturing process. On the other hand, in a manufacturing method of a rechargeable lithium-ion battery of this invention, since a solid electrolyte is directly formed on an electrode material of an anode and/or a negative electrode, since it is not generated, problems, such as handling independently, can be made still thinner.

[0015]

In a rechargeable lithium-ion battery of this invention, a filmy solid electrolyte prepares a slurry which contains lithium ion conductivity crystal, glass, or crystallized glass as mineral matter, and can produce it by coating this slurry directly on an electrode material of an anode and/or a negative electrode.

[0016]

As a method of coating a slurry directly on an electrode material of an anode and/or a negative electrode, Printing technique, such as methods, such as dip, spin coating, and tape casting, an ink jet, and screen-stencil, can be used, and what distributed with a binder powder which has lithium ion conductivity in a solvent can be used for a slurry as mineral matter. As for mineral matter, it is preferred to consist of a crystal, glass, or crystallized glass. As for this filmy solid electrolyte, it is preferred to contain mineral matter 40% of the weight or more.

[0017]

Here, as for lithium ion conductivity powder to be used, it is preferred to have high lithium ion conductivity. It is stable crystallized glass chemically still more preferably, and mother glass is specifically the presentation of a  $\text{Li}_2\text{O}$ -aluminum<sub>2</sub> $\text{O}_3$ - $\text{TiO}_2$ - $\text{SiO}_2$ - $\text{P}_2\text{O}_5$  system, Heat-treat this glass, it is made to crystallize, and a main crystal phase in that case is the powder which is  $\text{Li}_{1-x+y}\text{aluminum}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$  ( $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ).

[0018]

Since a binder to be used makes an electrode which are a crystal, glass or crystallized glass powder, and a substrate bind, it is preferred to use a charge of an organic high polymer material. As a concrete material, polyethylene oxide, polyethylene, polypropylene, Polymer materials, such as fluoro-resins, such as polyolefine, polytetrafluoroethylene, polychlorotrifluoroethylene resin, and polyvinylidene fluoride, polyamide, and polyester polyacrylate, and a polymer material which has these as a structural unit can be used. Since the ion conductivity of a compound electrolyte will also become high if a polymer material which added lithium salt etc. and to which lithium ion conductivity was made to add is used or it uses a binder which has lithium ion conductivity, it is more desirable. As a solvent, an organic solvent which the above-mentioned polymer material dissolves or distributes can be used.

[0019]

In a rechargeable lithium-ion battery of this invention, a filmy solid electrolyte is also producible by coating lithium ion conductivity mineral matter directly on an electrode material. As a method of coating mineral matter directly on an electrode material, known thin film manufacturing devices, such as sputtering process, a laser ablation method, and a plasma metal spray, can also be used. Under the present circumstances, a thin film can be directly formed on an electrode material using a composite material which contained a lithium ion conductivity crystal, glass, or a crystal and glass of these lithium ion conductivity at a target.

[0020]

Here, it is preferred to use lithium ion conductivity stable and high crystallized glass for a target material chemically [ the above ]. When it thin-film-izes, it may become amorphous, but by heat-treating in this case and crystallizing, if the above-mentioned main crystal phase is deposited, it will be satisfactory. Mother glass before crystallization of this crystallized glass can be similarly used as a target. The above-mentioned main crystal phase is obtained by performing crystallization treatment, after forming membranes also in this case. A target of a composite material adds an inorganic binder to a lithium ion conductivity crystal, glass, and crystallized glass powder, calcinates it, and is obtained. As a crystallized glass granular material, it is preferred here to have lithium ion conductivity, and it is more preferred that a main crystal phase is  $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ . As mean particle diameter of this crystallized glass granular material, 5 micrometers or less are preferred, and 3 micrometers or less are more preferred. As for an inorganic binder to be used, it is preferred that it is a crystal and glass which are the inorganic oxides of a low melting point, and less than 20wt% of quantity is preferred.

[0021]

In a rechargeable lithium-ion battery using a thin film solid electrolyte of this invention, a thing in which material which contains a transition metal oxide as positive active material in aluminium foil as a positive pole collector,

etc. was formed can be used as an anode. As a positive-active-material material used for an anode of a rechargeable lithium-ion battery of this invention, An oxide which can use occlusion of lithium and a transition metal compound which can be emitted, for example, is chosen from transition metals, such as manganese, cobalt, iron, nickel, vanadium, niobium, molybdenum, and titanium, and which contains a kind at least can be used. When using for negative electrode active material material which does not contain lithium, it is preferred to use a lithium containing transition metal oxide.

[0022]

In a rechargeable lithium-ion battery using a thin film solid electrolyte of this invention, lithium ion conductivity mineral matter is contained in this filmy solid electrolyte, and it is preferred to contain lithium ion conductivity mineral matter as an ion conduction auxiliary agent also in an anode. It is preferred that a main crystal phase uses crystallized glass powder which is  $Li_{1+x+y} \text{aluminum}_x \text{Ti}_{2-x} \text{Si}_y \text{P}_{3-y} \text{O}_{12}$  as lithium ion conductivity mineral matter used here like mineral matter contained in this filmy solid electrolyte. As mean particle diameter of a crystallized glass granular material used here, 5 micrometers or less are preferred and 3 micrometers or less are more preferred.

[0023]

In a rechargeable lithium-ion battery using a thin film solid electrolyte of this invention, it is preferred to an anode to contain an electric conduction auxiliary agent and/or a binder. As an electric conduction auxiliary agent, acetylene black is preferred, and the polyvinylidene fluoride PVdF is preferred as a binder.

[0024]

In a rechargeable lithium-ion battery of this invention, a thing in which material which contains negative electrode active material in copper foil as a negative pole collector, etc. was formed can be used as a negative electrode. As a negative-electrode-active-material material used for a negative electrode of a rechargeable lithium-ion battery of this invention, Material of carbon systems, such as transition metal oxides, such as occlusion of lithium, such as metal lithium, a lithium aluminum alloy, a lithium indium alloy, metal and an alloy which can be emitted, titanium, and vanadium, black lead, activated carbon, mesophase pitch carbon fiber, can be used.

[0025]

In a rechargeable lithium-ion battery of this invention, lithium ion conductivity mineral matter is contained in this filmy solid electrolyte, and it is preferred to contain lithium ion conductivity mineral matter as an ion conduction auxiliary agent also in a negative electrode. As lithium ion conductivity mineral matter used here, It is preferred that a main crystal phase uses crystallized glass powder which is  $Li_{1+x+y} \text{aluminum}_x \text{Ti}_{2-x} \text{Si}_y \text{P}_{3-y} \text{O}_{12}$  like mineral matter contained in this filmy solid electrolyte. This negative electrode can be prepared by mixing negative-electrode-active-material material, an ion conduction auxiliary agent, and a binder using an acetone solvent, and applying this mixture on a negative pole collector. Commercial graphite powder can be used for negative electrode active material.

[0026]

A concrete example is hereafter given and described about a lithium ion battery using a thin film solid electrolyte and this concerning this invention, and a comparative example is given and a point that a rechargeable lithium-ion battery provided with a thin film solid electrolyte concerning this invention is excellent is clarified. A rechargeable lithium-ion battery of this invention is not limited to what was shown in the following example, in a range which does not change the gist, is changed suitably and can be carried out.

[0027]

[Embodiment of the Invention]

(Example 1)

(Production of an anode)

To positive active material, using commercial cobalt-acid-lithium  $LiCoO_2$ , this positive-active-material material, Acetylene black which is an electric conduction auxiliary agent, and the crystallized glass powder whose main crystal phase it is an ion conduction auxiliary agent and is  $Li_{1+x+y} \text{aluminum}_x \text{Ti}_{2-x} \text{Si}_y \text{P}_{3-y} \text{O}_{12}$ . The polyvinylidene fluoride PVdF which is a binder is mixed using an acetone solvent, After applying this mixture so that thickness may be set to about 50 micrometers on the 10-micrometer-thick positive pole collector which is an aluminium sheet, the positive electrode sheet which dried this at the temperature of 100 \*\* and became a sheet shaped was produced. Here, as crystallized glass powder, mean particle diameter used a 1.0 micrometer (volume average) thing, and the maximum droplet size used an 8-micrometer thing. Particle diameter was measured with laser

diffraction / scatter type particle size distribution measuring device.

[0028]

(Production of a negative electrode)

Crystallized glass powder which is this negative-electrode-active-material material and an ion conduction auxiliary agent using the graphite powder of marketing to negative electrode active material (as well as what was used for production of an anode) A main crystal phase is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$ , and 1.0 micrometer and a maximum droplet size mean particle diameter 8 micrometers, The polyvinylidene fluoride PVdF which is a binder was mixed using the acetone solvent, and after applying this mixture so that thickness may be set to about 50 micrometers on the 10-micrometer-thick negative pole collector which is a copper sheet, the negative electrode sheet which dried this at the temperature of 100 \*\* and became a sheet shaped was produced.

[0029]

(Production of a filmy solid electrolyte, and assembly of a cell)

A main crystal phase is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$ , and 0.15 micrometer and a maximum droplet size mean particle diameter 0.3-micrometer crystallized glass powder, Acetone was uniformly mixed for the polyethylene oxide which added  $LiBF_4$  as lithium salt as a solvent. The active material [ of the positive electrode sheet which produced this mixture above ], and active material side of a negative electrode sheet applied to each, and also acetone which is a solvent was dried and removed, and the filmy solid electrolyte layer was directly formed on the electrode material of an anode and a negative electrode. Where the spreading side of an anode and a negative electrode sheet is pasted together, it started in through and size of 40x50 mm at the roll press, and the rechargeable lithium-ion battery shown in drawing 1 in which the filmy solid electrolyte was formed between the anode and the negative electrode was assembled. The whole thickness of this cell was 110 micrometers, and the thickness of the filmy solid electrolyte layer was 3 micrometers in it.

The lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test of 25 \*\* and 4.2V-3.5V was done. The cycle characteristic of the service capacity to 20 cycles was shown in drawing 2. The initial service capacity of Example 1 is 36.2mAh, and after 20 cycles was maintaining 34.1mAh and not less than 96% of initial capacity.

[0030]

(Comparative example 1)

Except not using crystallized glass powder for a filmy solid electrolyte, the same cell as Example 1 was constructed, and the charge-and-discharge cycle test was done on the same conditions. The cycle characteristic of the service capacity to 20 cycles was shown in drawing 2.

[0031]

(Example 2)

Commercial cobalt-acid-lithium  $LiCoO_2$  is used for positive active material, The same positive-active-material material as Example 1, the electric conduction auxiliary agent, the ion conduction auxiliary agent, and the binder were mixed using the acetone solvent, this mixture was applied so that thickness might be set to about 50 micrometers on the 10-micrometer-thick positive pole collector which is an aluminium sheet, and it was considered as the positive electrode layer. after that -- immediately -- production of the filmy solid electrolyte of Example 1 -- the same -- the mixture of the polyethylene oxide which added crystallized glass powder and lithium salt was thinly applied on this positive electrode layer, and was made into the electrolyte layer.

Continuously, the same mixture as production of the negative electrode of Example 1 was applied so that thickness might be set to about 50 micrometers on an electrolyte layer. After pasting together to the negative-electrode spreading side the copper sheet which is a negative pole collector and making it dry at 100 \*\*, it started in through and size of 40x50 mm at the roll press, and the rechargeable lithium-ion battery shown in drawing 1 in which the filmy solid electrolyte was formed between the anode and the negative electrode was assembled. The thickness of this whole cell was 100 micrometers, and the thickness of the filmy solid electrolyte layer was about 2 micrometers in it. Since the spreading of an anode-electrolyte-negative electrode cannot enter a drying process on the way, in each interface, the anode, the solid electrolyte layer, and a solid electrolyte and a negative electrode layer have been mixed by it.

[0032]

The lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test of 4.2V-3.5V was done in the constant current of 25 \*\* and  $0.1 \text{ mA/cm}^2$ . The rapid charge-

and-discharge cycle test was also done in the constant current of 1 mA/cm<sup>2</sup>.

[0033]

(Comparative example 2)

Except not using crystallized glass powder for a filmy solid electrolyte, the same cell as Example 2 was constructed, and the charge-and-discharge cycle test was done on the same conditions. Comparison of 0.1 and the initial service capacity in the charge-and-discharge density of 1 mA/cm<sup>2</sup>, and the service capacity after 20 cycles was shown in Table 1.

[0034]

[Table 1]

	実施例2		比較例2	
	0.1mA/cm <sup>2</sup>	1mA/cm <sup>2</sup>	0.1mA/cm <sup>2</sup>	1mA/cm <sup>2</sup>
初期放電容量(mAh)	39.2	38.8	35.0	32.2
20サイクル後の放電容量(mAh)	36.3	35.1	31.2	26.5

[0035]

As shown in Table 1, the fall of the service capacity by degradation according [ the cell of Example 2 ] to a cycle and rapid charge and discharge was suppressed small.

[0036]

(Example 3)

The same crystallized glass powder as what was used for production of the anode of Example 1 (a main crystal phase is  $Li_{1+x+y}Al_{x}Ti_{2-x}Si_yP_{3-y}O_{12}$ , and) After mean particle diameter carried out pressing of the 1.0 micrometer to the shape of a disk by using lithium phosphate  $Li_3PO_4$  as an inorganic binder, it was calcinated and obtained the target material. The periphery and both sides of the target material which were acquired were ground and ground, and the sputtering target (100 mm in diameter and 1 mm in thickness) was obtained.

[0037]

With RF magnetron sputtering equipment, the thin film was formed on phi20mm and the 20-micrometer-thick lithium aluminum alloy foil of a negative electrode. The solid electrolyte layer obtained at this time was 0.1 micrometer in thickness. Next, on this filmy solid electrolyte,  $LiCoO_2$  which is a positive electrode material was formed with the sputter device. The positive electrode film obtained at this time was 2 micrometers in thickness. Aluminum which is a positive pole collector on it was formed in thickness of 0.1 micrometer. Since the solid electrolyte and the positive electrode film were made amorphous, they heat-treated at 550 \*\* and were used as the thin film cell about 22 micrometers thick. This cell was pierced to phi18mm, and it put into the phi20mm coin cell, and finished setting up a coin type cell.

[0038]

-The charge-and-discharge cycle test of 3.5V-2.5V was done according to the constant current of 1 mA/cm<sup>2</sup> at each temperature of 20 \*\*, 25 \*\*, and 80 \*\*. The coin type cell which it finished setting up was mounted in the circuit board by a 250 \*\* solder reflow, and the same cycle test was done at 25 \*\*.

[0039]

(Comparative example 3)

The cell as for which the electrolyte impregnated the nonwoven fabric with the electrolysis solution as usual was produced. The anode formed  $LiCoO_2$  with the sputter device like Example 1 on the 10-micrometer aluminium foil in thickness using the lithium aluminum alloy as Example 1 with same negative electrode. An anode and a negative electrode are pasted together via the separator of a 26-micrometer-thick nonwoven fabric. It impregnated there with the propylene carbonate which added  $LiN(C_2F_5SO_2)_2$  as a lithium supporting electrolyte, was considered as the filmy cell about 58 micrometers thick, and finished setting up a coin type cell like Example 3 except the

above. The charge-and-discharge cycle test was done on the same conditions as Example 3.

Comparison of the service capacity after the first stage after the initial service capacity at each temperature, the service capacity after 300 cycles, and a solder reflow and 300 cycles was shown in Table 2.

[0040]

[Table 2]

	実施例3		比較例3	
	初期容量 (mAh)	300Cycle 後 の容量 (mAh)	初期容量 (mAh)	300Cycle 後 の容量 (mAh)
-25°C	0.12	0.11	0.05	0.02
25°C	0.22	0.20	0.22	0.16
80°C	0.24	0.19	0.22	0.12
25°C (ハンダリフ ロー)	0.21	0.18	破裂	-

[0041]

From Table 2, the cell of Example 3 has a good cycle characteristic at each temperature, and was maintaining about 50% of capacity also in -25 \*\* as compared with room temperature use. Although the cell of the comparative example 3 exploded by a solder reflow, the cell of Example 3 hardly caused capacity deterioration.

[0042]

(Example 4)

(Production of an anode)

The positive electrode layer and the thin electrolyte layer were produced on aluminum of a positive pole collector like Example 2 except the point of having used  $\text{LiMn}_2\text{O}_4$  for positive active material.

[0043]

(Production of a negative electrode)

Use  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  for negative electrode active material, and This negative-electrode-active-material material, The polyvinylidene fluoride PVdF which is a binder is mixed with the crystallized glass powder which is an ion conduction auxiliary agent using an acetone solvent, This mixture was applied so that thickness might be set to about 50 micrometers on the 10-micrometer-thick negative pole collector which is a copper sheet, and the negative electrode layer was produced on copper of a negative pole collector. after that -- immediately -- production of the filmy solid electrolyte of Example 1 -- the same -- the mixture of the polyethylene oxide which added crystallized glass powder and lithium salt was thinly applied on this negative electrode layer, and the thin electrolyte layer was produced.

[0044]

(Assembly of a cell)

Both the electrolyte sides of an anode and a negative electrode are pasted together, at 100 \*\*, it let it pass to the roll press, and it was dried. The thickness of 60 micrometers and a filmy solid electrolyte layer of the thickness of the positive electrode layer was 100 micrometers in thickness of 3 micrometers and a negative electrode layer, and the whole thickness was about 180 micrometers. It started in size of 40x50 mm, the lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test of 3.0V-2.2V was done in the constant current of 25 \*\* and  $0.1 \text{ mA/cm}^2$ .

[0045]

(Comparative example 4)

Except not using crystallized glass powder for the electrolyte layer of an anode and a negative electrode, the same cell as Example 4 was constructed, and the charge-and-discharge cycle test was done on the same conditions. The cycle characteristic of the service capacity to 20 cycles was shown in drawing 3. Although the

initial service capacity of Example 4 was a value somewhat lower than the comparative example 4, there was little degradation of a subsequent cycle characteristic and 20 cycles after was maintaining 98% of early capacity.

[0046]

(Example 5)

The same cell as Example 4 was produced and the charge-and-discharge cycle test of 3.0V-2.2V was done at 25 \*\* by the rapid charge and discharge of the constant current of  $0.1 \text{ mA/cm}^2$  and 1, and  $3 \text{ mA/cm}^2$ .

[0047]

(Comparative example 5)

Acetone is uniformly mixed for crystallized glass powder and the polyethylene oxide which added  $\text{LiBF}_4$  as lithium salt as a solvent. This mixture was applied to a thickness of 50 micrometers on the cast sheet, this was dried, it applied to the roll press, and the sheet shaped 30-micrometer-thick solid electrolyte was produced. The negative electrode layer was produced on the positive electrode layer and the negative pole collector of a copper sheet on aluminum of a positive pole collector like Example 4. And the positive electrode layer and the negative electrode layer were pasted together to both sides of a sheet-shaped solid electrolyte (separator), it applied to the roll press, and the sheet shaped 210-micrometer-thick cell was produced. It started in size of 40x50 mm, the lead was attached to the positive pole collector and the negative pole collector, and the charge-and-discharge cycle test was done on the same conditions as Example 4. Initial service capacity and the service capacity after 20 cycles were shown in Table 3.

[0048]

[Table 3]

充放電密度	実施例5		比較例5	
	初期容量 (mAh)	20Cycle 後の容量 (mAh)	初期容量 (mAh)	20Cycle 後の容量 (mAh)
$0.1 \text{ mA/cm}^2$	32.0	31.3	30.8	29.0
$1 \text{ mA/cm}^2$	32.0	31.1	25.3	23.1
$3 \text{ mA/cm}^2$	31.5	30.3	20.4	16.5

[0049]

Although there was no difference at the charge-and-discharge speed about  $0.1 \text{ mA/cm}^2$  with a big cell of Example 5 and the comparative example 5, when charge-and-discharge density was raised and rapid charge and discharge were performed, reduction of capacity carried out clearly has been checked by the comparative example 5. This is the cause that resistance of the ion migration in the interface of the anode-solid electrolyte of a cell and a solid electrolyte-negative electrode is big. The solid electrolyte was directly formed in the electrode and the cell which is equal also to a big output was obtained in Example 5 which reduced interfacial resistance.

[0050]

[Translation done.]

**\* NOTICES \***

JPO and INPI are not responsible for any  
damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

**[Brief Description of the Drawings]**

[Drawing 1] The section explanatory view showing the internal structure of the rechargeable lithium-ion battery of this invention.

[Drawing 2] Change of the service capacity accompanying the charging and discharging cycle of the rechargeable lithium-ion battery obtained by Example 1 and the comparative example 1.

[Drawing 3] Change of the service capacity accompanying the charging and discharging cycle of the rechargeable lithium-ion battery obtained by Example 4 and the comparative example 4.

**[Description of Notations]**

1. Positive pole collector
2. Anode
3. Filmy solid electrolyte
4. Negative electrode
5. Negative pole collector

---

[Translation done.]

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

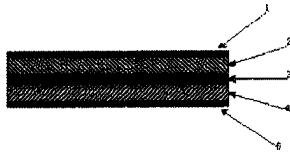
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

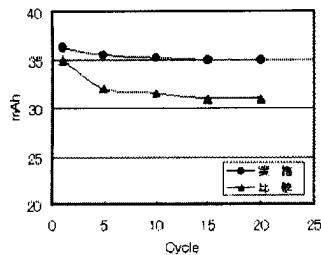
DRAWINGS

---

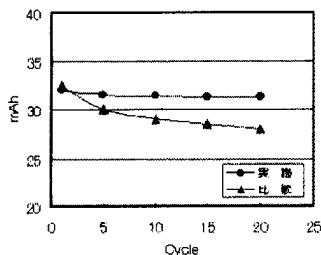
## [Drawing 1]



## [Drawing 2]



## [Drawing 3]



---

[Translation done.]

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

WRITTEN AMENDMENT

[Written amendment]

[Filing date] November 25 (2003.11.25), Heisei 15

[Amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] 0040

[Method of Amendment] Change

[The contents of amendment]

[0040]

[Table 1]

	実施例 3		比較例 3	
	初期容量 (mAh)	300Cycle 後の容量 (mAh)	初期容量 (mAh)	300Cycle後 の容量 (mAh)
- 20°C	0.12	0.11	0.05	0.02
25°C	0.22	0.20	0.22	0.16
80°C	0.24	0.19	0.22	0.12
25°C (ハンダリ フロー)	0.21	0.18	破裂	-

---

[Translation done.]